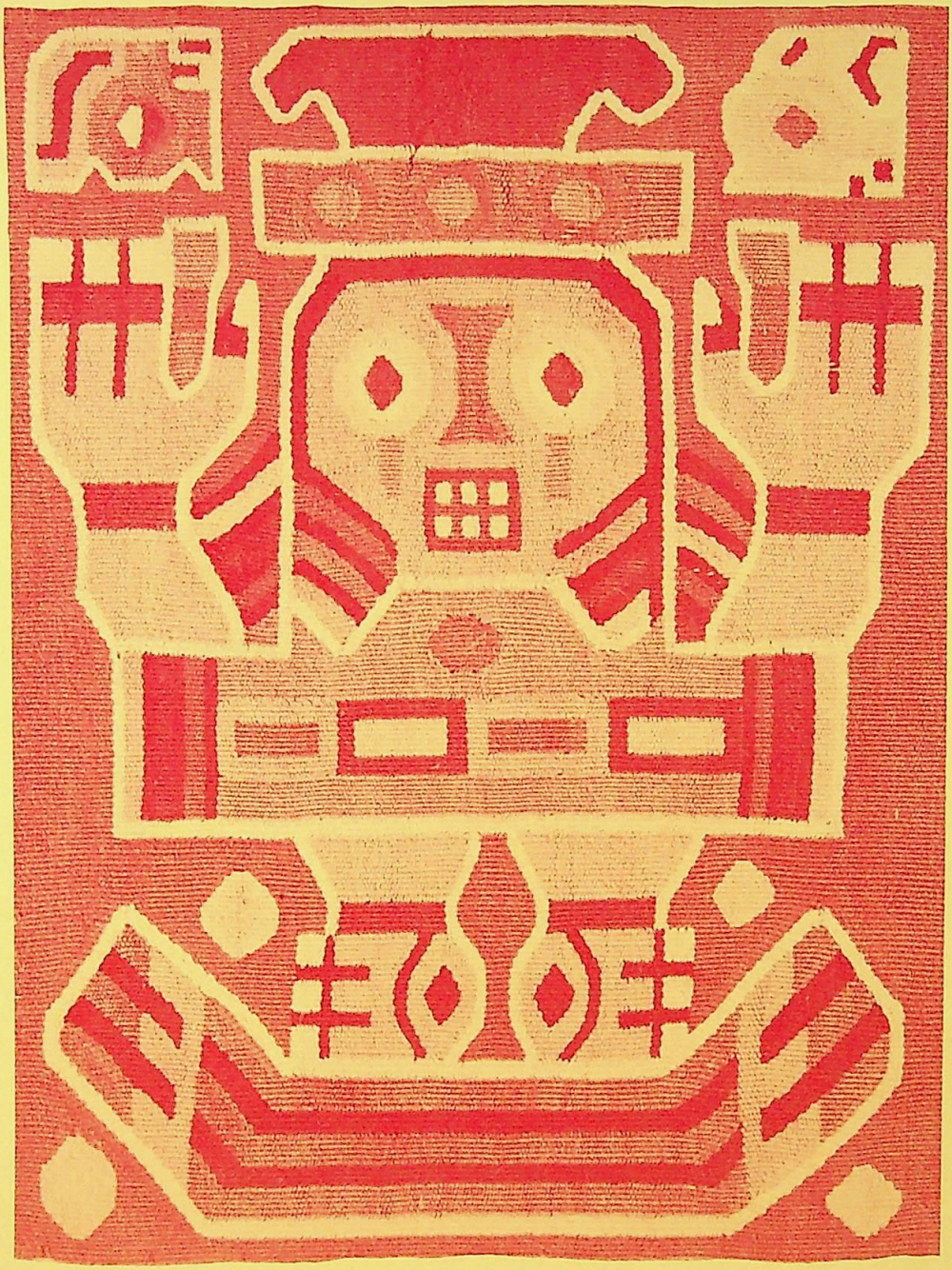
TEXTILE MUSEUM JOURNAL



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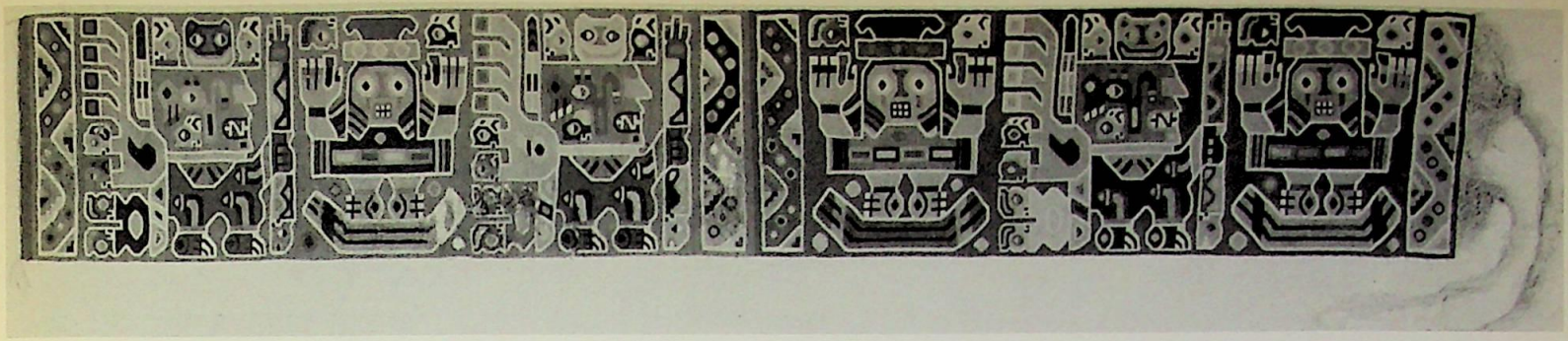

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COVER: Detail of interlocked tapestry band (illustrated in full above). Alternating winged messengers holding staffs, and frontal human figures standing on balsa rafts (?). Classic Tiahuanaco. Coyungo, Rio Grande Valley, Peru. About A.D. 900. Textile Museum 1965.32.1. On view in the Ancient Peruvian Textiles Exhibition through April 15, 1967.

DRAWINGS by Milton Franklin Sonday, Jr.

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PRINCIPLES OF TEXTILE CONSERVATION SCIENCE NO. VII

CHARACTERISTICS OF DETERGENTS FOR CLEANING HISTORIC TEXTILES

JAMES W. RICE

What Soap or Detergent Is Best for Cleaning Old and Fragile Textiles?

This is a question often asked of the staff of our Conservation Department. For reasons of policy and fairness, we cannot recommend specific brand names but we can provide the inquirer with advice and ideas that will help him to recognize the special requirements for many of the usual problems and teach him how to select and use these cleaning agents. This we hope to do in the following discussions and illustrations.

What Is a Detergent?

This is another natural question. Broadly defined a *detergent* is a substance that will increase the effectiveness of a cleaning fluid. It describes many chemical compounds and mixtures such as alkalies or the abrasives, pumice and rouge or special solvent additives like pine oil or kerosene. But for the purposes of this discussion we will limit the term to the *soaps* and the modern substitutes therefor, the *synthetic detergents* or SYNDETS, an abbreviation used by many writers. Both of these belong to a special class of SURFACE ACTIVE AGENTS usually written SURFACTANTS for short. Not all SURFACTANTS are good detergents but all *detergents* must produce certain surface activity change effects if they are to be satisfactory cleaning aids. These were mentioned as adverse characteristics of a special but most common class of insoluble soils in No. V of this series of technical papers [1] and will be explained and illustrated in more detail as this article develops. Briefly stated, the *surface activity* effect results expected from a detergent or *soap* are (a) increases in wetting, (b) spreading of the cleaning medium, (c) penetration, (d) reduction of size and mass of the particles, (e) maintenance of deflocculation of particles, (f) suspension, and (g) protective lubrication of the fabric.

What Characteristics of Surfaces Are Important in Connection With Detergency?

Perhaps a description and some imaginary pictures of our conception of the appearance of the surfaces we are to deal with will be helpful in presenting these several *surface activity effects*. In the first place, the surfaces that we encounter are the INTERFACES between two or more different but adjoining substances. In some instances there is an attraction between the substances and in other cases they will repel one another.

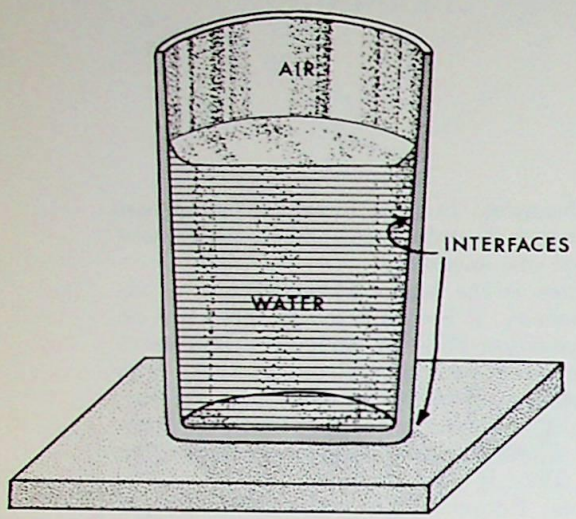
The interface is the boundary between two adjoining substances. If both are solids, there will be a definite separation between surfaces unless there are attraction forces such as electromagnetic or Van der Waal's effects. Between liquids and solid surfaces, this special separation becomes exceedingly small except where there is repellency between the substances. This is the case also between two liquid surfaces. Between a gas and a solid or a gas and a liquid, molecules or atoms join tenaciously to the surface. Two gases will mix and there will be no interface. The purpose of the *surfactant* is to change the space effects or the forces that keep the two substances apart. Figure 1 shows the *interface* between water and a glass container and illustrates limited attraction of the glass for water. Figure 2 illustrates repellency between the glass and mercury. Figure 3 shows the interface between water and a particle of soil. From these illustrations we may conclude that the first step in changing surface activity is that of reducing the interfacial resistance. This we call *wetting*.

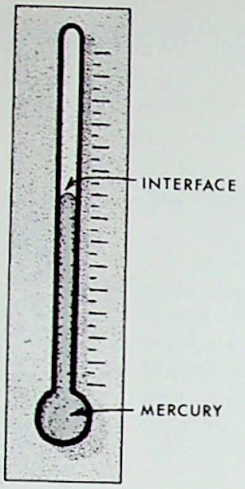
What Is Wetting?

Wetting is the process of bringing two surfaces closer together. Actually there are two surface activity mechanisms involved. One is concerned with reducing the internal attraction between molecules of a liquid cleansing medium adjacent to a surface and the other with causing the liquid to spread over that surface. The first of these is called *surface tension lowering*, and is explained by the following diagrams and discussion.

How Can Surface Tension Be Visualized?

Surface tension is best illustrated by the classic experiment of floating a needle on the top of pure water. If done carefully, the needle will remain on top (see Figure 4) until the surface breaks. The needle cannot float, however, if any substance is dissolved in the water that weakens the internal attraction between the liquid molecules. This is a case of using a wetting agent to lower the resistance of the liquid surface to penetration. This same surface tension also accounts for the tendency of water to form nearly spherical droplets in falling. When





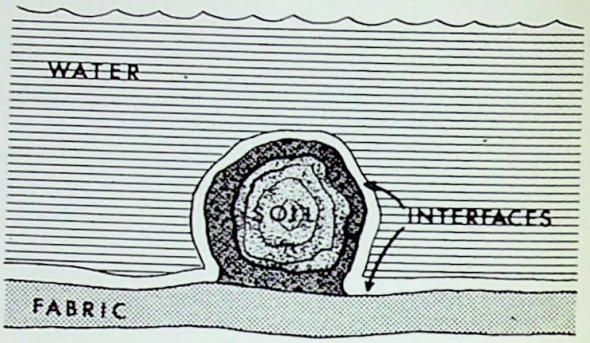
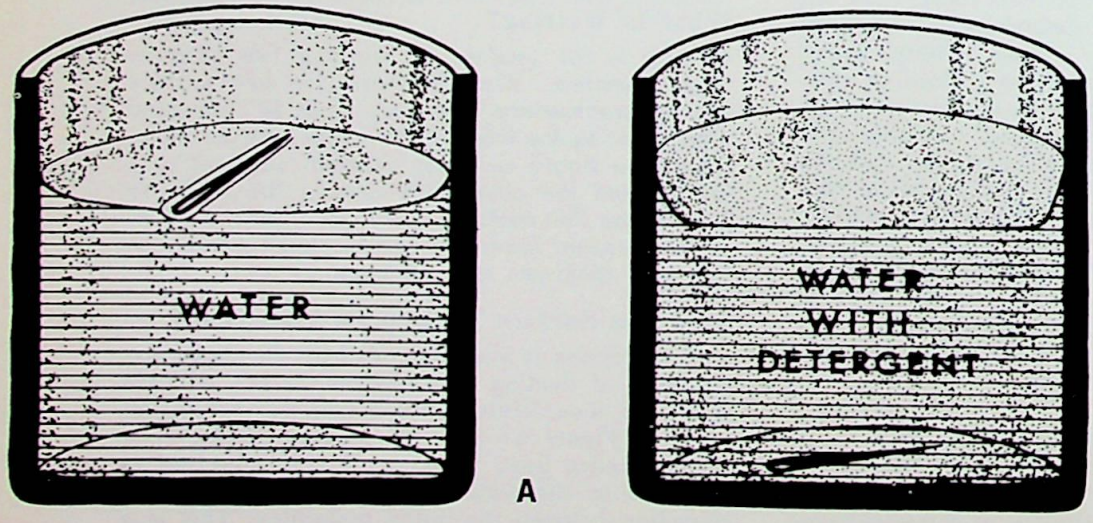


Figure 1 (left) *Water wets glass and rises along sides (attraction)*

Figure 2 (center) *Mercury does not wet glass and drops along sides (repellency)*

Figure 3 (right) *A diagram of a particle of soil surrounded by a sticky, greasy film in contact with pure water*



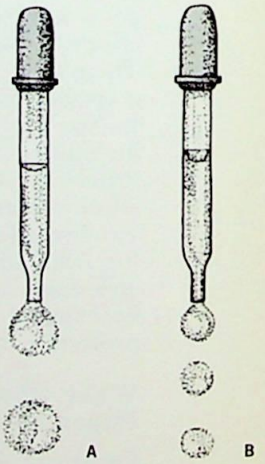


Figure 4 (left) *Surface tension lowering:* (a) *In pure water the needle floats—surface tension great.* (b) *A little soap is added and the needle sinks—surface tension less. Note spreading effect at interface of glass and water-detergent* (b)

Figure 5 (right) (a) *Pure water—large drops;* (b) *Water and detergent—small drops*

a surface tension lowering agent is added, the droplets are much smaller. The sketches of the two pipettes in Figure 5 show this effect.

How Does Spreading Appear?

If a drop of water is placed on a Saran*[2] film surface, it will form a flattened sphere which will roll around if disturbed. If a drop of oil is put on another place on the Saran*[2] the liquid will spread out and if disturbed, flow, leaving behind a film of the oil. A very small amount of wetting agent in the water will cause it to do the same. The oil appears to be more strongly attracted to the surface than the water alone. If the liquid film spreads very thinly over a very large area, we may conclude that *adsorbtion* is taking place. This means that one or more parts of the molecules of the liquid or fluid become attached to the surface. The attractive forces causing this effect may be either *electro-magnetic* or *mutual affinity* between different molecules which, however, contain identical subgroups or *radicals*. As we progress in our study of *surfactants,* we will have occasion to use either one or both of these theories to explain and help in planning their use.

In the case of many SUBSTRATES or surfaces to be acted upon by the *surfactant,* the *wetting agent* is apparently adsorbed because of the mutual affinity effect. According to the usually accepted picture of this adsorbtion case, the individual molecules are attached to the surface at one end, while the rest of the molecule extends out. Thus, where we are considering the actions of a true soap as wetting agent, and where the shape of the molecule is known to resemble a rather rigid chain-like structure represented by a straight line thus ————, we would have a furry deposit resembling the sketch in Figure 6. When this occurs, the molecules are said to be *oriented. Wetting* with water does not occur, however, unless the other end of the molecule will attract and hold water molecules. It has been found that groups or radicals that contain the element oxygen will usually attract one or more molecules of water which also is composed of oxygen together with hydrogen, with a structure shape represented by H—O—H. When the molecule contains a water resembling radical, we call it an *hydrophilic* or water attracting group. The other end is the *hydrophobic* or water rejecting group. Such a detergent molecule is customarily represented thus ————● in explanatory diagrams where the ● stands for the water resembling group. The *hydrophilic* part of the HOH molecule then may be represented as ————● where the HOH stands for one or more molecules of water attached to it. With the help of these simple symbols, we may imagine the progress of wetting to go like the next two figures where Figure 7 emphasizes the interfacial zone between a substrate that is essentially hydrophobic and the surface of pure water. After a wetting agent is added, the surfactant molecules orient themselves to the surface and the width of the interface zone is materially reduced, if it does not disappear. From this diagram, one may deduce that a wetting agent of short molecular structure will bring the water closer to the surface than a long one.

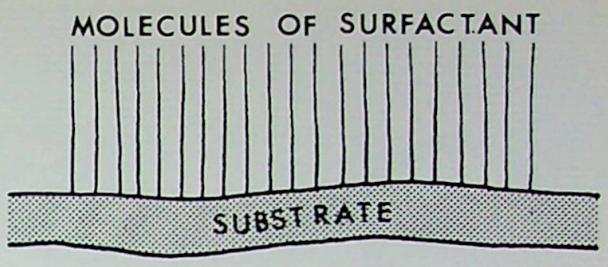


Figure 6 *Surface orientation of molecules on spreading*

Why Is Penetration Necessary in Removal of Soils?

Wetting, while very important as a preliminary step in cleaning, is only one of the surface action effects. The next thing is to penetrate between the soil and the substrate so as to overcome any adhesion or interfacial attraction. Also very many substances, especially soils, are amorphous (noncrystaline) and porous. These pores may vary in size from exceedingly tiny, that can only be detected by X-ray magnification techniques, to those that may be seen by the naked eye. Penetration in this case is required for breaking up large soil masses. Exposed surfaces probably accept surfac-

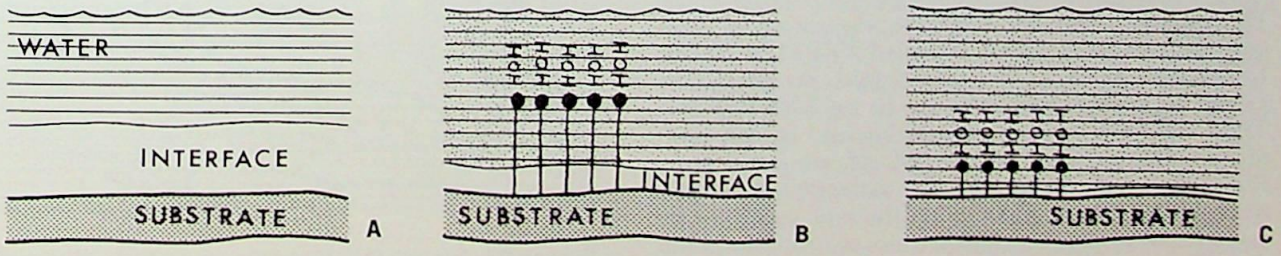


Figure 7 (a) *No wetting agent, interface much exaggerated.* (b) *Effect of a fair wetting agent but good detergent, interface very small.* (c) *Effect of a very good wetting agent but poor detergent, interface practically disappears*

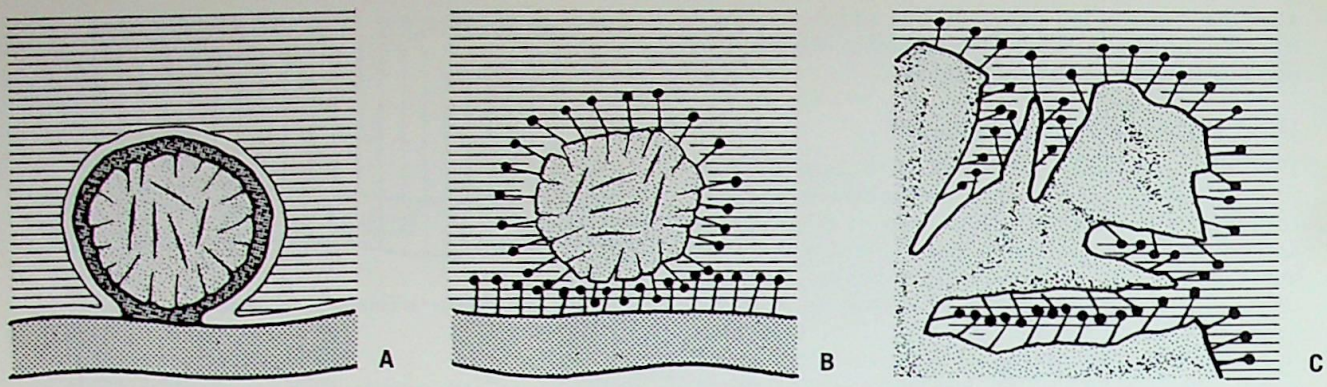


Figure 8 (a) *A porous soil particle adheres to the surface.* (b) *Surfactant molecules from the detergent solution penetrate the area of adhesion and orient themselves on surfaces.* (c) *Section of* (b)*—surfactant molecules from the detergent solution enter pores and orient themselves on surfaces*

tant molecules immediately but these may not be adsorbed into the pores without other help. Two common ways of assisting penetration are by heating the solution and by stirring or agitating the bath so as to exchange fresh solution for spent liquid near the action scene. Figure 8 presents an imaginary mass of soil under attack at the interface of the substrate and within the pore structure by surfactant molecules.

How May the Disintegration of a Soil Mass Be Accomplished?

Of course, many soil deposits can be pulverized by rubbing, tamping, or grinding but as a rule mechanical treatments of the sort are unwise for older textiles. While it is seldom possible to dispense with mechanical manipulation of the fabric altogether, damage may be minimized by what the author believes to be the next thing that happens in the detersive process. This is a continuation of the theory of wetting. Once the surfactant molecules are oriented on the pore surfaces, water molecules are attracted to their hydrophilic ends. In effect, this causes a swelling action which is powerful enough to dislodge or split the soil particle. Figure 9 is an attempt to show how crowding of water molecules by attraction into a confined space may bring about this disruptive effect.

Once Reduced in Size, How Can These Fine Particles Be Kept Apart?

The process of maintaining the separation of fine particles within a liquid is called PEPTIZATION. Under the same conditions, liquid droplets dispersed in another liquid would be an EMULSION. There are two ways of doing this and in the case of the best detergents both effects are employed. First, the chain length of the surfactant molecule must be long enough to push the soil particle far enough away from the substrate so that the Van der Waal's adhesive attraction between different substances no longer holds. This idea is illustrated by the drawings in Figures 8, 9, and 10. In these, it may be seen that an emulsifier of short molecular length might be desirable for a cosmetic cream for example, but not for a textile cleanser.

The second way of maintaining separation depends on the principle of *electrostatic repulsion*. For this the chemist selects or constructs a detergent with a molecule that is strongly *polar*. By this we mean that one end of the molecule must bear a strong electrical charge. The more common soaps and very many of the Syndets are of this nature. In these, the *hydrophilic* group contains a strongly positive element such as Sodium (Na^+) or Potassium (K^+) which causes that end to become electromagnetically positive. At the same time, the *hydrophobic* end becomes negative in charge. In this case

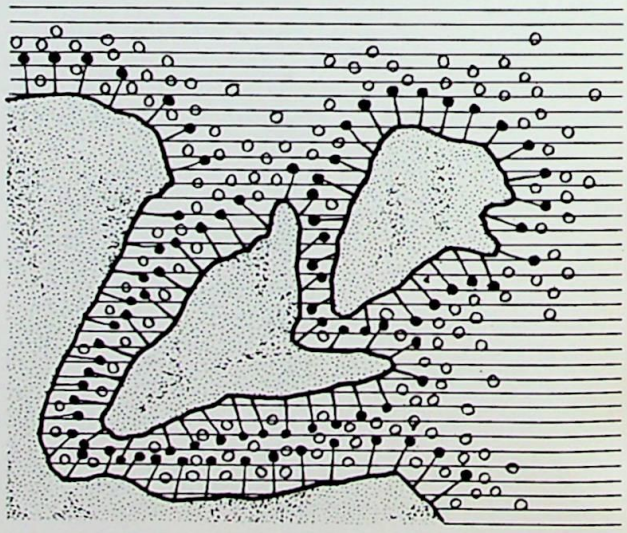


Figure 9 *Attraction of water* (0) *to the hydrophilic ends of the surfactant molecules* (0) *results in swelling of the pores and disintegration and fragmentation of the soil*

the detergent molecule may be represented thus —————●⁺. Since like magnetic charges repel one another, the effect of a soap or detergent on soil particles and substrates is as shown in Figure 11, where the negative hydrophobic ends are attracted to the soil and the fiber surface, while the positive hydrophilic parts are oriented away from it. These like molecular ends will then repel similarly surfactant protected particles and prevent them from coalescing.

How Is Suspension Maintained After Soil Particles Are Separated?

After *peptization* or *emulsification*, the heavier particles must not settle out until removal has been completed. Our next problem, then, is how may they be suspended within the solution until they can be flushed away? *Suspension* may be accomplished by one or both of two *colloidal* effects, and may be explained in part, when we recall the tendency for large molecules to collect into micelles, especially when the limit of solubility of the surfactant is just exceeded. We should also bear in mind that these solubility limits can be changed by raising or lowering the temperature or by pH or ionic concentration changes. Since some of the surfactant will have already been adsorbed on the particle surface and will have attracted molecules of water, we may imagine that the immediate surface complex will approach the specific gravity of water and thus the particle will become more buoyant. Figure 12 may clarify this supposition.

The second theoretical case of suspension deals with larger soil masses such as may be seen without high magnification. Examples are fragments of fibers and undissolved dye particles from strongly colored top dyeings. These may be floated by large

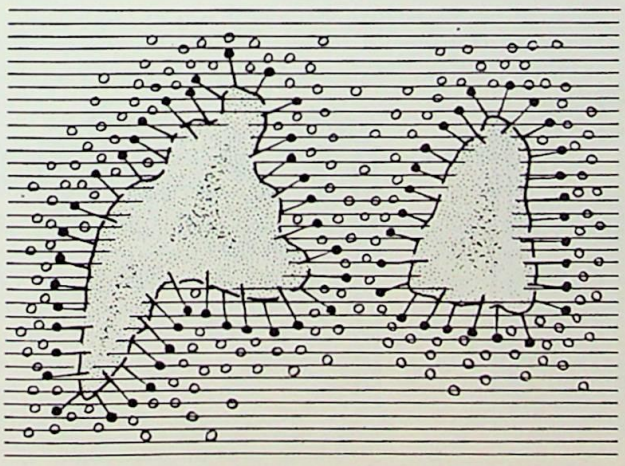


Figure 10 *Disintegration completed; separated particles form a jelly, or cream-like emulsion. Van der Waal's effect no longer holds*

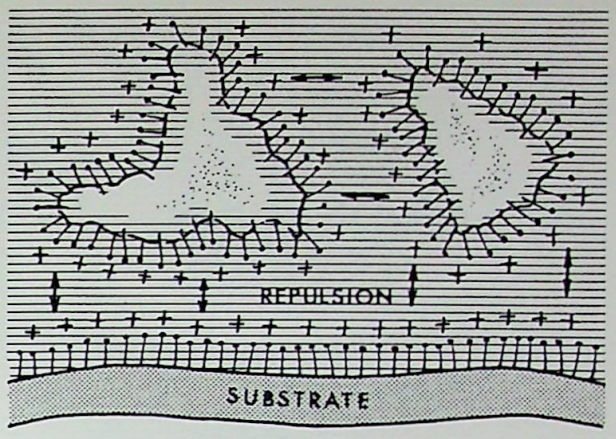


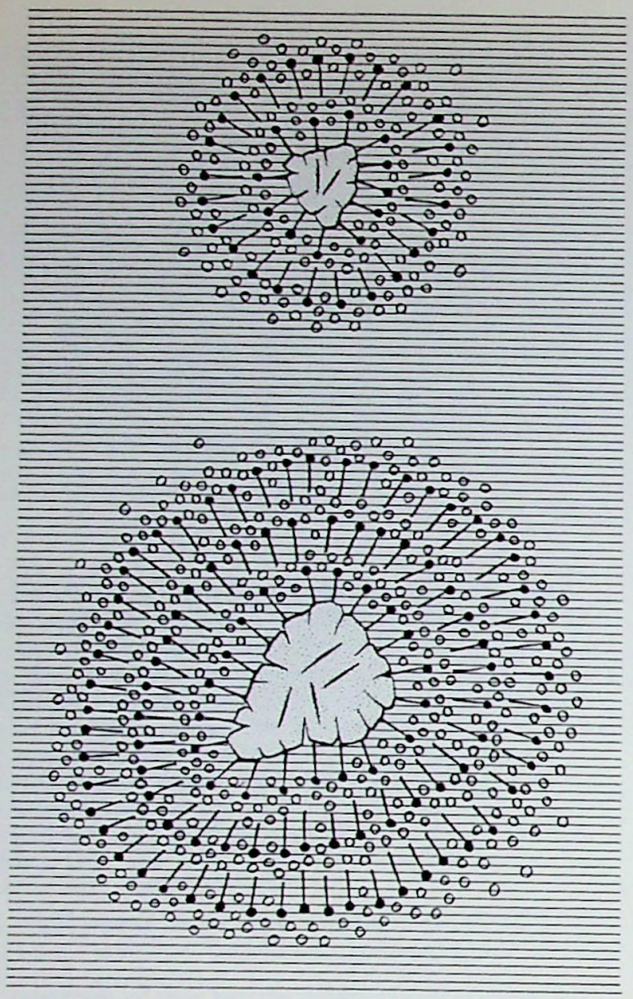
Figure 11 *Electrostatic repulsion*

gel-like surfactant and water groupings similar to the sketches in Figure 13, or continuous surfactant and water films surrounding air bubbles as in a foam or lather, as illustrated by Figure 14.

A moderate quantity of lather is usually indicative of excellent suspension of the soil because of the presence of the necessary micelles. However, it is possible to have so many micelles that free molecules are not able to function in the manner explained previously. When this happens, cleaning effectiveness drops.

What Is Solubilization, and How Does It Affect the Cleaning Problem?

SOLUBILIZATION, which should not be confused with dissolving of substances in a solvent, is a special case of *micelle* action. It happens when a soil, such as an oil or grease, does not dissolve in water but when a very small amount of certain special detergents is added to the water, the oil is first dissolved in the detergent, which in turn is dispersed in the form of very small micellar complexes within the water. In this event, the detergent molecule is of such a nature that it will probably attract only one molecule of the oil but can attract more than one molecule of the water. Figure 15 represents our concept of how one or more molecules of a modern dishwashing detergent with a molecule of a grease and several molecules of water might form a relatively stable complex. A micelle of this size would be small enough to be dispersed in the water so thoroughly that it might be difficult to distinguish it from a dispersion of individual molecules in a solvent. Micelles of this sort are different from those of the suspension or lather types where thousands of molecules may be involved. The *solubilization* phenomenon is one way of explaining the effectiveness of soaking baths in cleaning work. It is especially important in the cleaning of dye stains and in those cases where the fabric may be too weak to withstand mechanical action.



How May Lubrication Be Accounted For?

Lubrication is one of the most commonly seen surface action phenomena but we seldom have occasion to think of just what may go on when surfaces are to be protected from abrasion or from sticking to one another.

Observation of the behavior of a good lubricant will show that it will spread over a surface and form a protective film. If we examine the chemical compositions of the better ones, we find that they are usually long chain organic compounds. While lubricant molecules do not necessarily have to have hydrophilic ends, one end at least must develop a strong attraction for surfaces that are not compatible with water. In this respect they will collect on the surfaces of metals and other water opposing substances and, as they do, will orient themselves with one end attached to that surface while the other end is free. These in turn attract other of the lubricant molecules, as explained by the micellar attraction theory, to increase the thickness of the film. This increase, however, provides for a flowable zone of the lubricant, which in turn overcomes sticking and adhesion of other nearby surfaces. Figure 16 may clarify this explanation.

Figure 12 (above) *Suspension of small soil particles within the detergent solution. As the water shell becomes larger, the apparent specific gravity is lowered*

Figure 13 (below) *A large particle of soil may sink because its apparent specific gravity is great compared to water, but with the attraction of more molecules of detergent forming a hydrated shell, micellar formation causes apparent specific gravity to become lowered and the soil more buoyant*

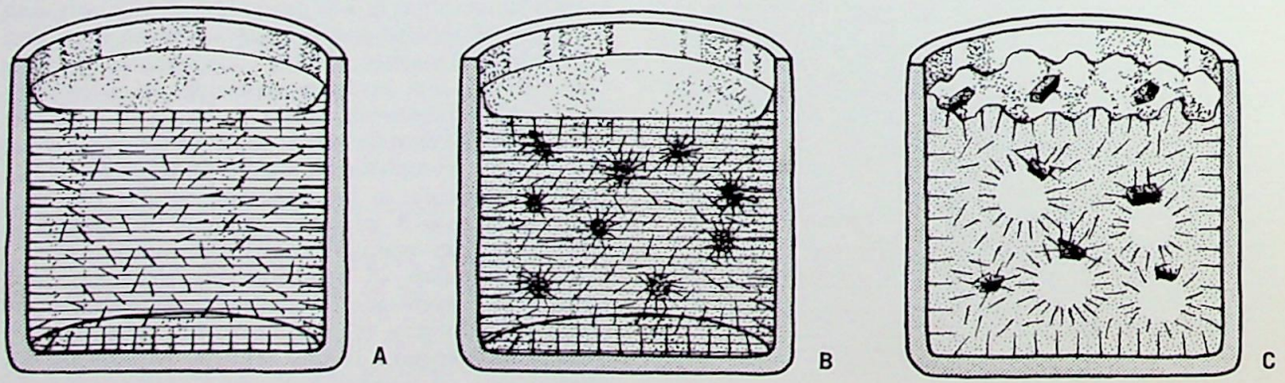
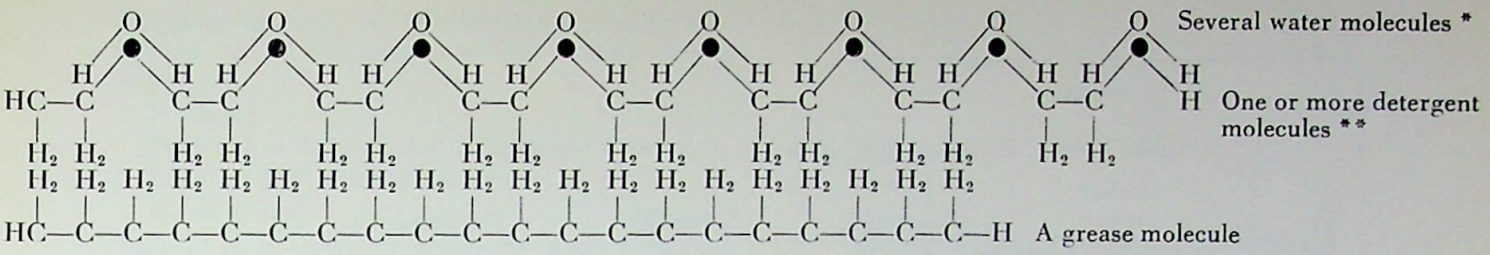


Figure 14 (a) *A diluted solution of singly dispersed molecules may not suspend large soil particles.* (b) *A more concentrated solution containing some micelles will do better.* (c) *A stable foam or lather indicates presence of extensive micellar films*



* The structural groups —C(=O)—C— resemble those of water H—O—H and will attract at least eight molecules of the latter. (This is probably by H bond formation such as is shown as follows: C(H)—O:H:O:—C(=O)).

** The structural groups —C(H₂)— in the detergent and the grease likewise attract one another and this may account in part for the solubility tendency of the two.

Figure 15 *An imaginary micelle complex in solubilization*

What Other General Qualities Besides the Surface Activity Effects Discussed Up to This Point Are Necessary For a Useful Detergent?

Perhaps the most important characteristic is that of limited solubility. Others are compatibility with acids, alkalies, metallic ions, oxidizing agents (bleaches), reducing agents (strippers), chelating or sequestering agents, enzymes, and special solvents. All of these will have a bearing on the choice of the surfactant and will also vary according to the soil, the substrate or surface and the cleaning medium.

We hope, in the following discussion, to provide a guide for basing a choice of a detergent or cleaning agent out of more than 3,000 listed in literature.[3]

Why Is Limited Solubility Necessary in a Detergent?

Solubility may be defined as mixing of molecules of one substance, a SOLUTE, in another, a SOLVENT. In the most simple case, the molecules are singly dispersed throughout the mixture which is called a SOLUTION. However, we may also have a colloidal solution which is a stable distribution of micelles within the mixture. As a rule, small molecules are more easily dispersed in the solution than large molecules. The smaller molecules do not collect into micelles readily and as these are necessary to a certain extent for good cleaning, especially where insoluble soil is concerned, we choose an agent that is not too soluble so that these micelles

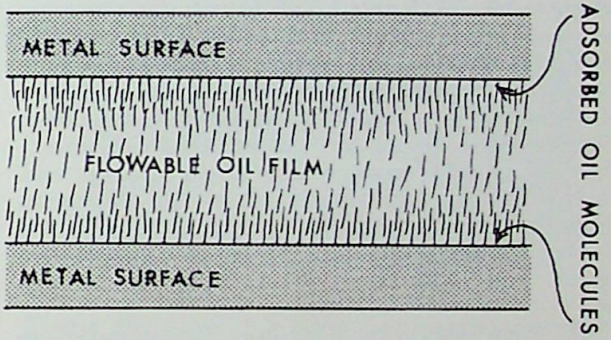


Figure 16 *Lubricant at work*

may be able to form. On the other hand, if the surfactant molecule is too large, not enough single molecules will be available to engender wetting, penetration, and protective spreading.

What Are Some of the Things That Affect the Solubility of the Detergents?

The shape of the detergent molecule and the attraction dissimilarity of the ends has been discussed already. Other influencing characteristics of these molecules are:

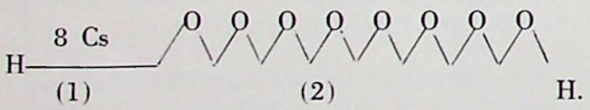
1) The chain length is important. If less than 10 carbon atoms long, it may be too soluble to form useful micelles. If more than 18 carbon atoms long, the substance is, unless chemically modified in some other way, too long and large to be soluble at reasonable working temperatures. The following

Table I may illustrate this point:

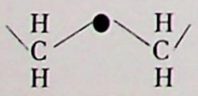
Carbon atoms	Diagram	Solubility	Predicted use
8	—●	in cold water	wetting, emulsifying
10	——●	cool water	salt water detergent, emulsifier
12	———●	tepid water	detergent for wool, fair cleaner
14	————●	120° F	toilet soap, good cleaning
16	—————●	140° F hot water	linens, etc. very good cleaning
18	——————●	160° F	greasy cottons, excellent cleaning
20	———————●	insoluble in 200° F	lubricant

2) The above generality about the length of chain does not hold good for unsaturated molecules where there are double bonds between one or more pairs of carbon atoms. In this case, an unsaturated chain detergent is more soluble than a similar saturated chain compound. As an example, a sodium oleate soap $C_{17}H_{33}COONa$, an unsaturated chain, dissolves in cooler water (about 20°-30° F lower) than its saturate counterpart sodium stearate soap $C_{17}H_{35}COONa$. Structurally, these two detergents differ in that at a particular point in the chain the oleate contains a double bond between two carbon atoms and with two fewer hydrogen atoms: ———C=C———COONa.

3) Some detergents have even longer molecules than the 18 carbon stearate used as illustrations shown in Table I. In this case, the continuity of carbon chain is interrupted at intervals by oxygen or some hydrophilic group. An example might be an ethylene oxide condensate of a form something like the following diagram:



In this case, group (1) is hydrophobic and consists of a succession of CH_2 units, whereas group (2) is hydrophilic and partly hydrophobic and consists of



units.

How Are Detergents Generally Classified?

According to their ionic activity in solution, detergents are classified into three groups:

1) Anionic detergents in which the hydrophilic end of the molecule is positive and is usually pictured as explained previously by the diagram symbol ———●$^-$ Na^+. Soaps are of this class.

2) Cationic detergents, wherein the hydrophilic end bears a negative charge and the molecule is pictorially represented by this diagram: ———●$^+$ Cl^-.

3) Nonionic detergents which bear no electrical charges and whose molecules are represented simply by ———●.

A solution of an anionic detergent in an electrolytic cell will deposit a slimy coating on the anode or positive pole as shown in the illustration, Figure 17. A cationic detergent will produce a similar effect on the cathode or negative electric pole of an electrolytic cell as in Figure 18. A nonionic detergent forms no deposits because of the electrophoresis effect and both electrodes of the cell will remain clean, as Figure 19 indicates. The significance of these three classes will be explained later in this discussion.

What Are the Most Commonly Encountered Classes of Anionic Detergents?

Detergents wherein the hydrophilic end of the molecule is negatively charged make up the great majority of the cleaning aids used today. All of them are man-made or synthetic, although the soaps are mistakenly not so considered because they can be produced accidentally. Usually all the anionic types are subdivided into two well known classes: true soaps and synthetics, but we prefer to consider them as chemical family groups. Although there are about

forty-four of these, we will, for this particular discussion, reduce this number to four simpler classes as follows:

1) Soaps,
2) Alkyl or fatty alcohol sulfates and sulfonates,
3) Alkyl-aryl sulfonates, and
4) all others.

Each of these classes or groups has some favorable and some adverse characteristics which will be brought out under the next several headings.

What Are Soaps?

In practice, soaps are formed whenever animal or vegetable fats and oils are brought together with a soluble base or alkali. This is the basis for soap manufacture and also is the reason why either ammonia or washing soda are so effective for cleaning greasy articles. In one case, the soap is made to be used later and is usually purified and refined while in the other event, the soap formed merely assists in the cleaning effect at the scene of cleaning action.

The natural animal or vegetable fats are compounds of glycerine and fatty acids and in soap manufacture glycerine is a valuable by-product which is separated and recovered. This does not happen when the soap is made as a step in cleaning. Actually, the soap is a chemical compound resulting from reacting a fatty acid with an alkali.

Fatty acids are long chain (10 — 18 Cs) hydrocarbons usually ending with the organic acid group —C(=O)—OH. The fatty acid (————COOH) is not soluble in water but will dissolve in many drycleaning solvents. When a fatty acid combines chemically with alkalies such as potassium, sodium and ammonium hydroxides and some of the organic bases related to ammonium, water soluble soaps result. Chemists call this particular reaction SAPONIFICATION. These several metallic ions bear strong positive electrical charges and in consequence confer anionic properties to the molecule in addition to water solubility. Thus schematically the fatty acid ———COOH in contact with Na OH (sodium hydroxide, a very common alkali) produces by saponification ———$COONa^+$ or simply ———●$^-$ Na^+ (anionic detergent).

What Is the Effect of Hard Water on Soap?

Almost all other metals and some other organic bases when combined with fatty acids form insoluble compounds in water. This explains the effect of hard water on soapsuds. In this case, soluble minerals such as calcium magnesium or ferrous iron ions in the hard water are exchanged for the alkali metal ions, potassium, sodium or ammonium, of the soaps to form insoluble metallic soaps which we see as sticky deposits on basins, fabrics, or floating on the rinse water. Other less common metals such as copper, zinc, and aluminum will do the same thing.

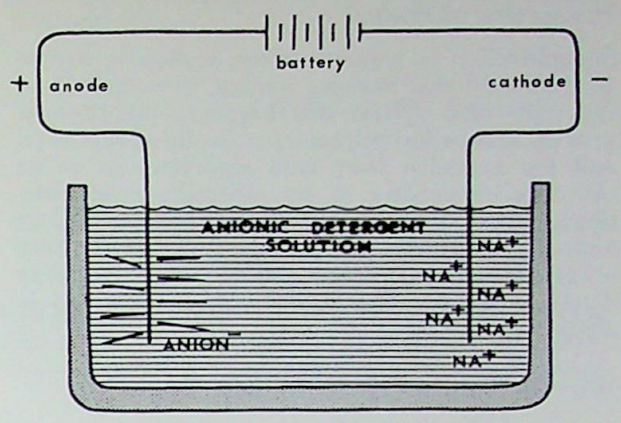


Figure 17 *Action of anionic detergents in an electrolytic cell*

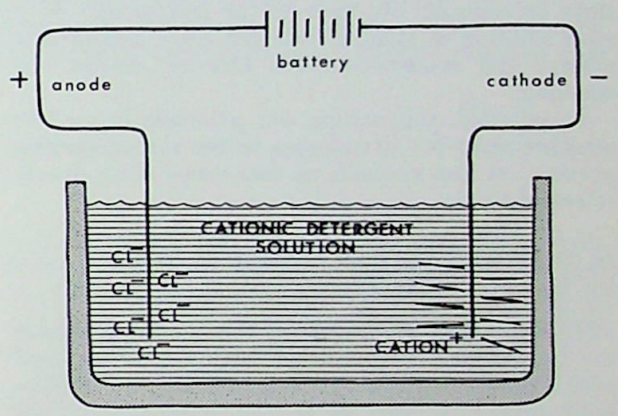


Figure 18 *Action of a cationic detergents in an electrolytic cell*

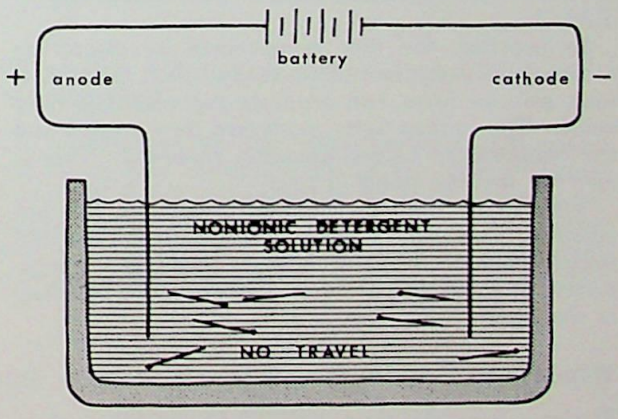


Figure 19 *Nonionic detergent molecules are not affected by electrical currents*

Why Do Acids Change the Detergent Properties of Soaps?

Saponification is reversed when a soap is treated with an acid that is more ionized (stronger) than the fatty acid. When this happens, the stronger acid exchanges its hydrogen ion for the alkali metal and the insoluble fatty acid separates out as an oily film. According to our schematic representation, a soap ————COONa$^+$ comes in contact with H$^+$ (acid) resulting in ————COOH (fatty acid) not soluble in water and no longer providing detersive action. This explains why soaps fail in acidic waters.

Why Is Soap Affected By Salt Water?

Molecules of soaps, other detergents and dyes in solution are profoundly affected by addition of salts to the mixture. These salts, of which sodium chloride (common table salt) as in sea water, and sodium sulfate or "Glaubers' salts," are widely used for dye setting and will bring about the collection of molecules into micelles and in this way cause them to separate out as a gel or precipitate. In a soap solution or suds, a little salt brine will greatly change the molecule-micelle balance needed for cleaning.

In practice, this *salting out* principle is used to separate soap out of solution in the manufacturing process. It also reminds us that soaps clean poorly in sea water.

In Describing a Soap, What Is Meant by the Term Titer?

TITER is a way of comparing the melting points of the fatty acid or mixture of fatty acids that compose a soap. High titer describes a soap made from fatty acids that melt at a high temperature. The resulting soap requires hot water to dissolve it and provide the best working temperature. A low titer soap is made from fatty acids that melt at relatively low temperatures and will work at moderate temperatures. It is related to molecular chain length, as has been explained before and illustrated in Table I.

In practice, the titer is obtained by dissolving a sample of soap in hot water and then treating it with acid to form and separate the resulting fatty acids. The molten fatty acids are then cooled and the temperature of solidification recorded. This is also the melting point or titer.

Very many high or medium titer soaps are not suitable for cleaning wools because shrinkage and felting may occur at such high washing temperatures. At these temperatures, excessive dye bleeding is also likely.

What Is a Neutral Soap?

We may hear the term NEUTRAL SOAP used to describe one that is reasonably safe for use on undamaged or new wool or on some dyes. Actually, if the pH of a soap that has been precisely saponified in manufacture is measured, we find that it will be alkaline, perhaps with a pH of 10 or slightly above. This may be explained by the rule of hydrolysis of salts or substances formed from strong alkalies and weak acids which says that these will be alkaline in solution.

Because of this effect, the so-called NEUTRAL soaps may produce bleeding of some sensitive dyes or promote shrinkage in fine woolen goods even though used at relatively cool temperatures.

Some soaps are deliberately made of an excess of fats over the exact amount needed for a neutral soap. These are known as SUPERFATTED SOAPS and are often found in special leather cleaners, and preservatives and lubricants.

As a rule, soaps work best at moderately high pH levels, ranging from over pH 10 to pH 12. This is accomplished by adding an excess of certain alkaline salts known as *builders*. The products are called BUILT SOAPS.

BUILT SOAPS are effective detergents for difficult and very greasy soils and stains, especially when used in hot water. They will produce shrinkage and wool fiber damage and excessive bleeding of many dyes and for these reasons are not recommended for many textile cleaning jobs.

The alkalinity of soaps, especially of the built variety will promote eventual yellowing and brown stain development in white cellulosic textile fibers. This discolor also results in dulling many colors in older specimens. This is due to the effect of alkalies on oxidation of cellulose and also because these soaps and the builders are hard to rinse out completely and remain on the textile unless neutralized or soured. Upon souring, the fatty acids remaining behind act as greasy adhesives for reception of resoiling.

What Causes Rancidity in Soaps?

Rancidity or development of objectionable odors does not happen to all soaps. Only those that contain unsaturated fatty acids which have been mentioned previously in this article are liable to give off odors on ageing. Some natural fats and oils that may be used in soaps that may turn rancid are olive oil, linseed oil, lard oil, cotton seed oil, tung oil, and fish oils.

The development of rancidity is at a double bond between two carbon atoms which is easily oxidized through stages of peroxide formation at this point. In turn, there is a fragmentation of the molecule with a resulting ALDEHYDE formation. These aldehydes are of a family of odiferous substances, much resembling the essence of goat.

A few oils or fats that are composed chiefly of saturated fatty acids are coconut oil, palm oil and tallow. Soaps made from these are not likely to produce odors.

Possible rancidity is often disguised by addition of perfume to a soap.

Under What Conditions Would a Metallic or Insoluble Soap Be Beneficial?

Metallic soaps especially are often formed deliberately within a fabric for particular purposes. For example, alum deposited in the fabric will produce a water repellent finish after soaking in hot sodium stearate soap solution. An insoluble aluminum soap forms and, if calendered afterwards, a glazed surface can be produced. This may suggest a way of restoring chintz effects. Soluble copper and zinc salts, if impregnated into a fabric and followed by soaking in a soap solution, will produce a measure of fungus and mildew protection; while the copper soap is rated as the more effective of the two, its green color may be objectionable. The zinc soap, although less toxic, is white and has very good lubrication properties.

Soaps may be deposited in fabrics and by treatment with an acid can form a fatty acid in place, and which, if later treated with a basic dye, acts as a mordant, thus setting a waxy color, similar to wax crayons, in place. These would be dissolved by dry solvents.

What Are the Chief Characteristics of the Fatty Alcohol Sulfates or Sulfonates?

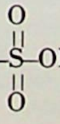
This particular chemical family of detergents approaches the cleansing action of soaps most nearly without being affected by those things that cause soaps to fail.

For example, compared on the basis of equal chain length, the F.A.S. which we may use to designate this particular group (Fatty Alcohol Sulfates or Sulfonates) is *a*, soluble at lower temperatures, *b*, not appreciably decomposed by acids, *c*, nearly neutral in pH, *d*, works best at a lower pH, *e*, less affected by salt brine, *f*, does not develop rancidity, and *g*, is not precipitated by water hardness ordinarily.

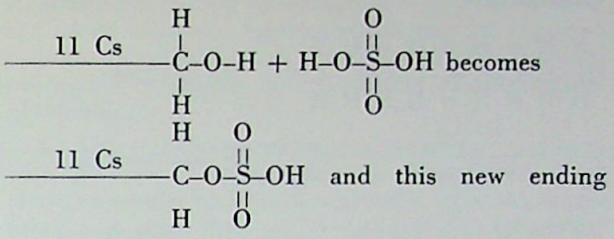
Like the common soaps, these synthetic detergents can be decomposed and broken down into non-toxic fragments which may be digested or utilized by living organisms.

What Is a Fatty Alcohol Sulfate or Sulfonate? (F.A.S.)

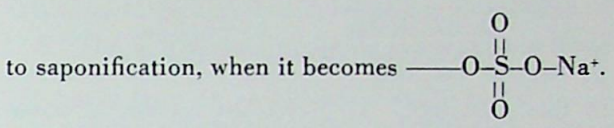
This group comprises synthetic detergents made by combining a fatty alcohol with sulfuric acid. Fatty alcohols occur less commonly in natural products than the corresponding fatty acids. They may be produced, however, by hydrogenation of fatty acids from vegetable and animal oils or as selected by-products from petroleum refining processes. Coconut oil, which is rich in lauric acid ($C_{11}H_{23}COOH$) is a common source. When hydrogenated, the lauric acid changes to lauric alcohol $C_{11}H_{23}CH_2OH$ which has very little hydrophilic properties but can react



with sulfuric acid H_2SO_4 ($H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$) to add the water attraction feature to the molecule. Thus our molecule

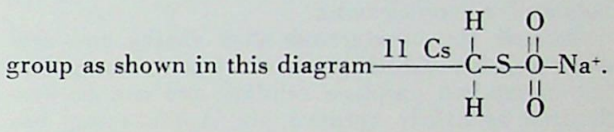


promises much hydrophilic activity. However, it is still not soluble in water nor is it electrically active until combined with an alkali metal in a similar way



to saponification, when it becomes ——$O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-Na^+$.

In this case we now have a typical F.A.S. detergent with the properties described. The hydrophilic end group described, $-OSO_3Na$ is known as a SULFATE. In some patented manufacturing processes the resultant surfactant has a slightly different end



group as shown in this diagram

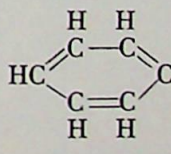
In this case the oxygen atom between the carbon chain and the end group is missing and the new detergent which is now called a SULFONATE is able to attract less water but otherwise is much like the sulfate.

Because competition in detergent manufacture has been so keen, many closely resembling chemical compounds have been synthesized and patented but for our purpose we may consider them as members of this class since they differ but very slightly in the several properties.

In general, the F.A.S. group detergents are suitable for cleaning of woolen goods and valuable textiles.

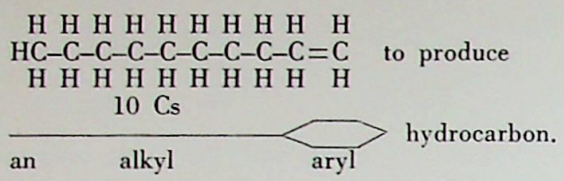
What Are Alkyl-Aryl Sulfonate Anionic Detergents?

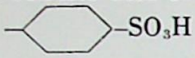
The Alkyl-Aryl or the Alkyl-Benzene Sylfonates which we may encounter under the abbreviations A.A.S. or A.B.S. are probably the most widely used detergents in the United States today. The term *aryl* in chemical language signifies a closed ring type of carbon compounds of which *benzene* C_6H_6



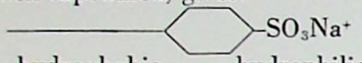
with a structural formula is the best known. This particular molecular structure is

quite reactive and may combine under proper conditions with an unsaturated alkyl or chain group, for example

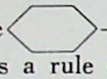


This in turn readily reacts with sulfuric acid to provide an alkyl-aryl-sulfonic acid 

which, when saponified, gives:



hydrophobic hydrophilic
or a sodium alkyl-aryl sulfonate.

In this case the 

section is water attractive and as a rule such a detergent is more soluble than a strictly alkyl or straight chain type of the same molecular length. For this reason this kind of molecule can be used with salt brines of relatively high concentrations, 5 or 10 per cent and will even require salt to produce a favorable micelle balance for good cleaning.

Because the unsaturated alkyl chains and aryl rings are abundant byproducts of petroleum cracking in modern gasolene refining and can be synthesized as briefly outlined, the A.A.S. group has been developed and marketed in great quantity. By selection of the chain length and by various modifications of the aryl group, unique characteristics of the molecules may be emphasized so that a wide choice of special agents is available, and at reasonable prices. This versatility in manufacturing has provided a wide variety of household and industrial detergents available today and by far the greater number of advertised products on the American market are of this class.

How Do the Cleansing and Other Properties of the A.A.S. Class Compare to the Soaps and F.A.S. Detergents?

Any comparison of this sort is necessarily a generalization because certain individual compounds may be particularly strong in some one of the various attributes of detergency. As a rule, however, these comments will hold:

1) As indicated by the molecular structure, they may produce more rapid wetting than the soaps or the F.A.S. types. For cleaning old or delicate fabrics this may not be desirable.

2) Their emulsification powers are probably equal to the first two classes.

3) The suspension, lubrication and protective powers are less than the soaps and F.A.S. types. These, of course, may be modified by additives such as salt and thickeners.

4) The classic hard water effects are not so apparent as in the case of soaps.

5) They are not acid sensitive in the pH ranges where soaps fail. Hence they can be used with acid dye-setting agents.

6) They are not alkali sensitive, especially at moderate pH levels up to about pH 10.5.

7) They are more soluble than soaps or the F.A.S. types. This means loss of soil suspension and protective lubrication effects but increases low temperature rinsability. This may be one of the reasons why they are popular for use in modern home laundry machines where most of the work is lightly soiled.

8) They may be used in sea water which definitely affects almost all soaps and to a lesser extent some F.A.S. detergents.

9) Some may be expected to be non-biodegradable, which means that they may form toxic substances by bacteriological processes. As a consequence, these A.A.S. types are accused of causing objectionable foaming and sewerage elimination troubles in some of our streams and it is possible that their use may soon be rigidly controlled by law.

What Are Some of the Characteristics of the Anionic Detergents That Do Not Fall Into the First Three Groups?

There are many individual substances and groups or families of chemicals that have specific useful properties in connection with textile treatments. Often they are wetting agents principally; others are mainly emulsifiers, solubilizers, foamers, or protective lubricants. Some are designed for use in dry-cleaning solvents and do not work in water alone.

About the beginning of this century these special detergents were usually discovered by accident, especially before surface activity factors were as well known as they are today. Now, however, they may be studied and planned on paper like an architect plans a building, long before the compound is ever made in a laboratory or produced in a factory.

Often these chemical compounds may be constructed of several shorter molecular structures combined to provide special disinfecting properties as in a dentifrice or a skin cleansing product. Others, such as hair shampoos which clean and lubricate at the same time, may be obtained. In nearly all these cases special uses are borne in mind and may only have an unusual application to textile conservation problems.

The anionic types have lent themselves to study and general usefulness so well that a great many more of these have been investigated and patented than either of the other ionic groups. For this reason, we may find individual detergents in other anionic chemical classes that have not been mentioned in our discussion but which may be tailored for some peculiar problem. In that event, the prospective user is referred for technical advice to manufacturers' literature or to encyclopedias or listings of detergents.

What Are the Chief Properties and Uses of the Nonionic Detergents?

As a group, the nonionic detergents have become popular and widely used in recent years. The following general comments illustrate the reasons why:

1. They are not affected by hard water or metallic ions in dilute solution. This might permit their use in cases where electrolytic cleansing action is desirable and where either anionic or cationic surfactants would interfere.

2. They are not affected by acids but may be insoluble in strong alkaline solutions.

3. They do not suspend heavy soils well but for increasing micellar concentrations of nonionics where heavy soil suspension is necessary, a nonionic thickener such as sodium carboxymethyl cellulose (C.M.C.) may be employed to overcome this defect.

4. They are very good solubilizing agents, especially for greases, waxes, and some dyestuffs and consequently are useful for soaking out otherwise unresponsive stains and spots.

5. They can be employed with either anionic or cationic detergents and are often mixed with one or another of these to increase the cleaning effect.

6. Many of the synthetic nonionic detergents are biodegradable and can be destroyed in sewage disposal systems.

7. Many individual nonionic detergents are low foamers and do not form stable suds. This is desirable in home laundering, and essential in machine dish washing.

8. Many nonionic detergents are soluble in cool or tepid water. This may be useful for cleaning woolens where shrinkage is undesirable.

What Are Some of the Nonionic Detergent Chemical Classes and What Are Their Special Properties?

As with other main detergent types, there are many individual substances that may not fall into a simple rigid classification. For our purposes, however, we will attempt to group them into four principal divisions to which many can be assigned. These are:

1. The saponins or natural detersive substances of which soap barks are examples. Other sources are nuts and fruits of certain plants. They have been used for cleaning purposes by primitive peoples in various parts of the world but, unfortunately, many of the different products are toxic and may cause undesirable health effects to the user. Extracts of some are useful drugs and under jungle conditions have been employed as arrow-tip poisons and stupifiers in stream waters for fish capturing. Detoxified but expensive extracts are rated as excellent cleansers. The chemical formulas and structure characteristics of these are quite complicated and may not resemble our ideal schematic detergent molecule.

2. The ethylene oxide fatty acid and fatty alcohol condensation types which have a schematic structure resembling this diagram ——●–●–●–●–● are useful nonionic agents, which may be expected to be biodegradable, and possess most of the general properties explained before. These are commonly obtainable.

3. The ethylene oxide condensation products with alkyl-aryl endings can be built from short chain molecules to form a schematic structure something like this ——⬭–O–O–O–O with many of the properties of the immediately preceding group. In this case, however, we might suppose that they would be non-biodegradable. We might also expect some of the longer chain members of this class to be excellent drycleaning detergents.

4. The fourth main grouping is assigned to those nonionic detergent molecules that are formed by joining a fatty or an alkyl-aryl chain to an *amine* (an organic substance related to ammonia). These are called amine CONDENSATES because in the synthesis, water is formed as a byproduct. Schematically, they will have a molecular form resembling the following diagram ——N(OH)H or perhaps ——N(●–●–●)H in which we have now introduced a nitrogen atom into the molecule. In this case, the compound can be readily made up from short chain fragments under proper chemical conditions and has hydrophobic-strong hydrophilic properties. This particular group possesses the same general properties as have already been enumerated. We would expect them to be biodegradable.

What Are the Chief Properties of the Cationic Surfactants?

The fact that this third main class of surfactants is electrically opposite to soaps and anionics has been brought out previously. They have useful distinctive behaviors which can be employed nicely in many conservation problems as may be seen in the following listing and discussions.

1. Although this class is not compatible with anionic detergents and cannot be used together with them, it may be mixed with nonionic types without loss of usefulness.

2. Cationic surfactants will exhaust out on fabrics and other surfaces, whereas the other types do not. This means that a solution of cationic agent will noticeably be much lower in concentration (percent still remaining in the liquid) after a short exposure. In the case of either anionic or nonionic agents, the change in solution concentration, because of the exhaustion phenomenon, is not so apparent. This peculiarity may help to account for some of the properties of this class.

3. The cationic types are widely employed for disinfection. They are very effective detergents for removal of slime growths and are useful for cleaning dairy equipment. They have also been used for sterilization of surgical instruments, hair dressing equipment and in sprays for deodorizing hospital rooms.

4. From the above, one may deduce that sewerage systems depending on bacteriological action might be poisoned by them.

5. Cationic detergents, as a rule, clean better under low pH or acid conditions than with alkalies. An excess of hydrogen ions would favor beneficial micelle formation.

6. Residual films from cationic surfactants have excellent anti-static properties. For example, if we treat plates of glass or sheets of plastic with a cationic agent and dry them, the plates or sheets will separate easily . Otherwise Van der Waal's adhesion may be so great as to prevent parting. In a similar fashion, a tangled fringe which would otherwise require much tedious labor for combing and separating will often fluff out on gentle shaking after a treatment with a cationic agent. This is also the principle of anti-static sprays for rugs.

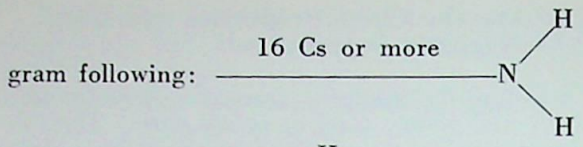
7. Cationic agents are effective setting agents for some dyes and colorants. Certain direct cotton dyes become more wash fast on being treated with such a surfactant. Another example is the precipitating effect of cationics on pigments used to color glass fibers and fabrics.

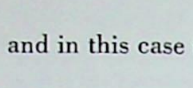
8. Very popular types of cationic detergents have been developed for use as fabric softeners especially for treating diapers. In this case, the agent exhausts tenaciously to the fabric to provide a soft lubricated texture. When we take into accout the bacteriocidal and deodorant properties too, its application in the last rinse in this type of cleaning is ideal. One drawback, however, is that the agents leave a natural yellow to tan color which is overcome by blueing. For this reason these commercial softeners come already mixed with a blue dye.

From the General Use Classification Point of View, How May the Cationic Surface Active Agents Be Divided?

A glance at the overall listing of the cationic properties suggests two main use categories. First, we have need for cleansing and lubricating agents. In the second place, we are concerned more with disinfectant requirements.

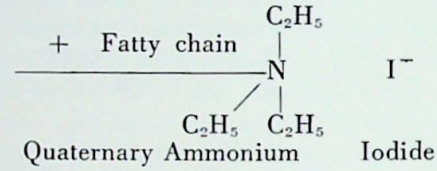
For those cleansing, lubricating and softening jobs we would expect a chemical molecule of a long chain fatty acid or fatty alcohol nature which could be manipulated chemically to form a weak positive ionic group when combined with a strong negative ion. For our first group, then, we select some compound of a class of chemicals known as *fatty amines* or *fatty amides*. Schematically, these fatty amines would appear somewhat like the diagram following:



and in this case the  group is hydrophilic.

The hydrophobic portion is actively attracted to surfaces with pronounced electro negative charges such as glass, metals and cellulose and for this reason will exhaust out and build up layers of fatty matter on such surfaces and give us valuable softening, lubricating and anti-static effects. But at the same time, these ion active coatings will attract negatively charged soil particles and hold them tenaciously. For this reason we may expect cationic treated fabrics or surfaces to resoil quickly.

The second main class of cationic surfactants is known as the QUARTERNARY AMMONIUM SALTS group. These resemble the fatty amines or amides in chemical structure except that the nitrogen atom in the chain has four filled valences instead of three when it reacts with the active acid.

Thus: 

Quaternary Ammonium Iodide

as an example provides both hydrophobic and hydrophilic properties. AMMONIUM type compounds ionize to a much greater extent than *amines* or *amides* so that an ionizable iodine ion I^-, in this example, may be easily formed. This is an active disinfectant. Other useful products of this main grouping may be *chlorides* or *bromides*.

Members of this main group are apt to be too soluble and too readily ionized to make good detergents but, for the reasons as this author sees them and has explained above, we would expect them to be very useful bacterial and fungicidal control aids.

How May These Theories Of Surface Action And Detergency Be Applied Towards Choosing Cleaning Agents For Specific Problems?

The detergent has much to do with the success of any cleaning operation, but how well it works can be modified by other factors such as water hardness, temperature, pH conditions, time, and the amount of mechanical action applied. All of these may be influenced by additives or by changing conditions of use at the operator's will. Factors that cannot be changed in any one problem are the substrate or fabric, the soil, and the colorant or dye. With these in mind, we will attempt to decribe what characteristics we would look for in certain general cases as is illustrated by the following:

CASE I *Greasy or oily substances* will generally

respond to anionic detergents, especially those that are or can be built to be strongly alkaline. Such detergents should have good penetrating and emulsifying powers. Suspension is subordinate to solubilization which is necessary for breaking up massive deposits. The excess alkali is useful for converting fatty acids and natural fats into soaps, which in turn contribute to the cleansing action. Since penetration depends on a relatively high ratio of free molecules compared to micelles, a high temperature is important. A medium or high titer soap will fit these specifications, especially if a little free alkali is added. This combination of high temperature and alkalinity is permissible for washing undyed, cellulosic fibers such as linens or cottons but would not be suitable for colored goods or protein fibers.

For these last conditions, one must substitute a solubilizing agent which will work in cool water. For colored cottons where dyes can be set by salt but where penetration of the oil may not be seriously affected thereby, an alkyl-aryl sulfonate type of synthetic detergent which is soluble at low temperatures would be chosen. There are many widely advertised products of this general type available on the American markets today, but out of these the user must choose one that is compatible with added salt or acids or both and which would still solubilize the oil without disturbing the dyestuffs. This probably is best done after a series of tests in miniature prior to cleaning.

Where acid conditions lower than about pH 3 or 4 are necessary to prevent dye bleeding, a nonionic detergent of the ethylene oxide fatty chain condensate type might not be affected but would be excellent grease solubilizer. Some of the "low foam" detergents recommended in advertisements for use in home laundry machines are of this kind.

When acid setting agents are demanded for cleaning soiled and greasy colored fabrics, sodium carboxymethyl cellulose or C.M.C., a thickening agent may be added to promote micelle formation suspension properties under adverse conditions.

CASE II Earthy mineral, matter such as clays and similar soils, constitute a difficult type of soil which varies in removal response according to how it may be deposited. If it settles on the fabric as an airborne dust or as a smeared contact, for example traffic dirt tracked on a carpet, the soil can usually be removed by an emulsifying and suspending detergent. Penetration and wetting is of less importance than where grease is the main ingredient. This action should take place at moderate or low temperatures to prevent solubilization of dyes. For this kind of work, fatty acid sulfates or sulfonates have been found to give good results. Alkyl-aryl sulfonates of the less soluble longer alkyl chains are also useful agents for this soil condition. Both of these classes are popular rug and carpet cleaning detergents, especially when built with polyphosphate salts to provide moderate alkalinity, pH 9 to 9.5. This produces a favorable micelle concentration as evidenced by a stable lather.

A second type of earthy mineral soils have already been described as extremely tiny particles.[1] These are often redeposited from muddy waters or dirty cleaning solutions. Removal in this event requires an agent which will penetrate into extremely fine fiber-pores and crannies and will have great selective affinity for the soil surface. Where these particle surfaces are negatively charged, as may be with metallic mineral ores or with glassy silicates, they will attract cationic surfactants strongly and if the detergent is one with a moderately long chain, a complex soil, surfactant-water, micelle may be formed which can be removed from the surface emulsified and suspended. Where such a cationic surfactant is adsorbed by the fibers, it may, if not removed, cause that substrate to resoil quickly. Rinsing with a nonionic detergent after cleaning should help to remove excess micelles of the adsorbed cationic agent and thus help to overcome this resoiling tendency.

Cationic fabric softeners and bacteriostats such as are advertised for treating baby diapers are available for the first stage treatment. One must be very careful in choosing a popular "low foam" rinsing agent because some of these are anionic in type and would not be compatible with the cationic soil remover.

These illustrations provide a guide for reaching decisions as to choice of detergents for particular problems. Once the type of detergent and the molecular construction and characteristics are determined in a particular case, special detergents may be found by consulting listings that may be obtained from soap and detergent manufacturing companies. An excellent guide for this purpose is found in a recently published Encyclopedia of Surface Active Agents.[3]

NOTES

[1] Principles of Textile Conservation Science, No. V, The Characteristics of Soils and Stains Encountered on Historic Textiles, James W. Rice, *Textile Museum Journal*, Vol. I, No. 3, 1964.

[2] *Signifies trade-marked products.

[3] See Vol. 1 and 2, Encyclopedia of Surface Active Agents, Sisley and Wood, Chemical Publishing Co., New York.

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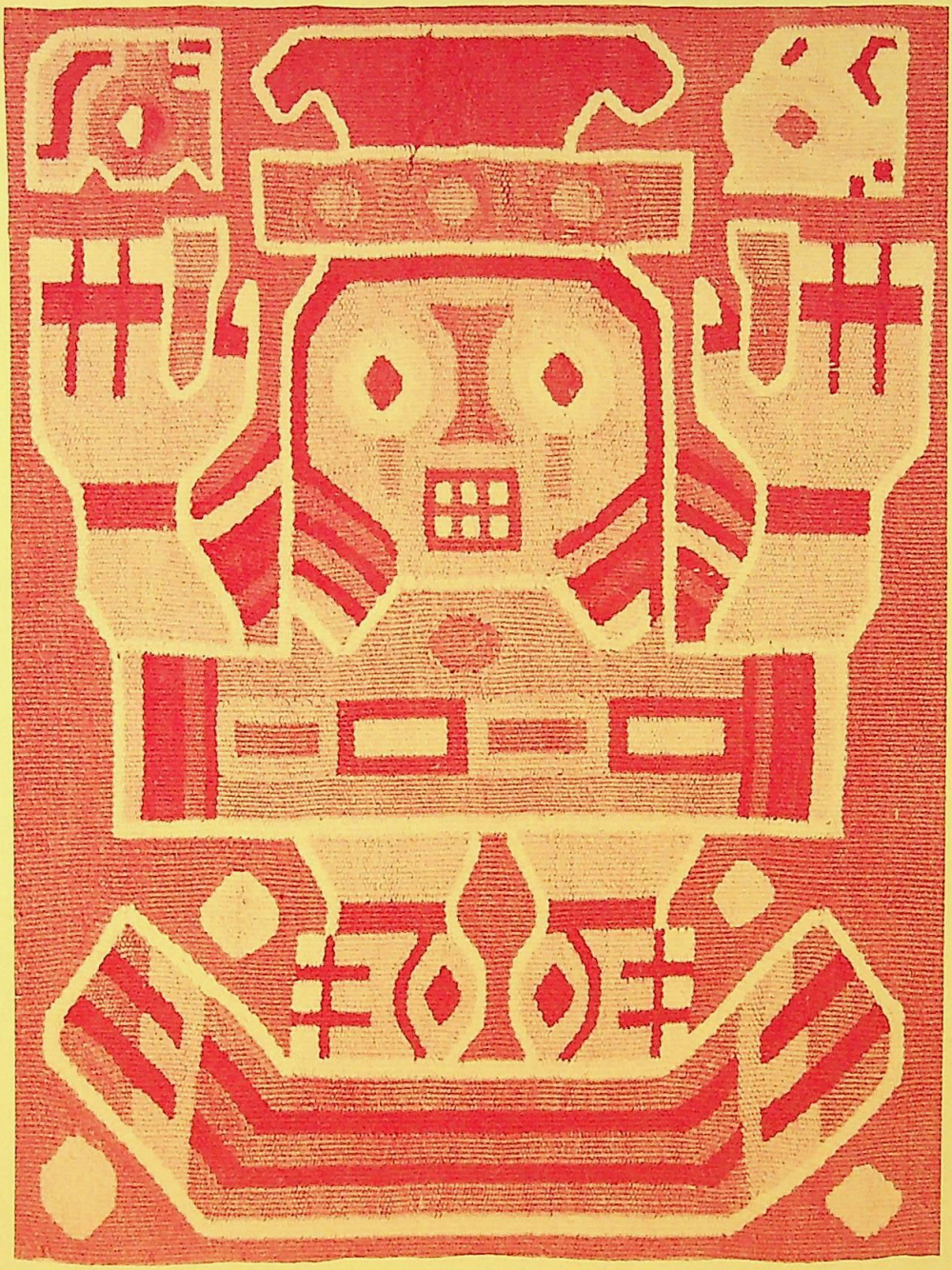

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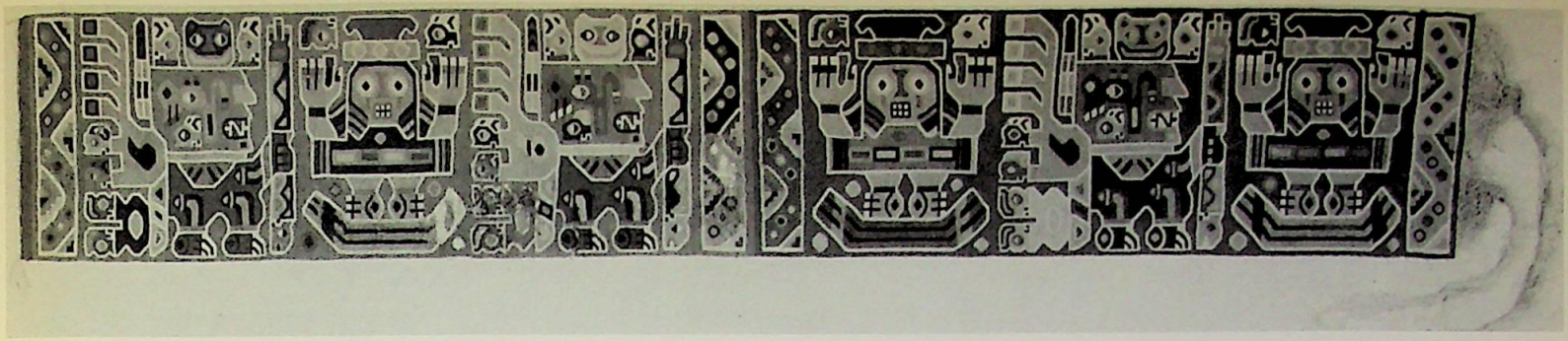

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COVER: Detail of interlocked tapestry band (illustrated in full above). Alternating winged messengers holding staffs, and frontal human figures standing on balsa rafts (?). Classic Tiahuanaco. Coyungo, Rio Grande Valley, Peru. About A.D. 900. Textile Museum 1965.32.1. On view in the Ancient Peruvian Textiles Exhibition through April 15, 1967.

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